Exchange with Deuterium and Isomerization of Some Alkenes Catalysed by Gallium Oxide

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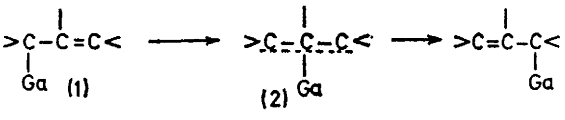
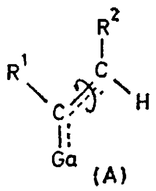
Summary Gallium oxide catalyses with high selectivity the exchange with deuterium of vinylic and allylic hydrogens in a variety of alkenes, and directly interconverts *cis* and *trans* isomers of butenes and pentenes at temperatures well below those required for double-bond shift.

Exchange with D_2 of vinylic hydrogens in alkenes is a selective, convenient reaction on Al_2O_3, but occurs on sites distinct from those responsible for double-bond migration.[1]

Unlike Al_2O_3, the catalytic activity of Ga_2O_3 depends upon loss of optimum amounts of O_2 (*ca.* $2{\cdot}4 \times 10^{12}$ molecules per cm^2 of surface). Samples with reproducible, high activity were prepared by evacuating 0·2 g Ga_2O_3 (spec. pure, $\leqslant$ 10 p.p.m. of other metals; Johnson Matthey Ltd.) at 290 °C for 10 min in a static reactor coupled by a capillary leak to a mass spectrometer. Standard reaction conditions were 230 °C, and 50·40 and 0·53 kNm^{-2} of D_2 and alkene, respectively. At 230 °C reactions were subject to diffusion control, except for ethylene which underwent simple exchange at a rate at least tenfold less than that of all other alkenes. Fast rates were deliberately chosen so that selectivities for exchange of different hydrogens could be monitored to high conversions in convenient periods. There was a very strong tendency for exchange to be confined to vinylic and allylic hydrogens in internal olefins, both cyclic and acyclic, and in 2-R-alk-1-enes (R = Me, Et). Typical results for cyclopentene (Table) show that 6 hydrogens only are readily replaced with increased selectivity at lower temperatures, and contrast with those obtained using an Al_2O_3 catalyst[2] which only exchanges the vinylic hydrogens.

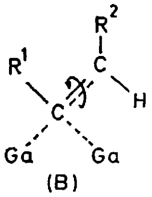


(1) (2)



(A)

or



(B)

However, exchange of n-alk-1-enes was more complex suggesting that double-bond shift was now important. Isomerizations of the n-butenes and n-pentenes were therefore studied using 0·2 g of Ga_2O_3, activated as before, with 1·33 kNm^{-2} of alkene in a static reactor (200 cm^3) coupled by a sampling valve to a g.l.c. unit. At 110 °C totally selective *cis* ⇌ *trans* interconversions of the alk-2-enes were readily obtained whereas, comparable rates of double-bond shift in the n-alk-1-enes being only achieved at 190 °C, giving initially equilibrium ratios of the alk-2-enes. Both the exchange reactions and isomerizations were severely retarded by D_2 indicating that the same sites are responsible for the two types of reactions.

Table

Distributions of deuterio-isomers of cyclopentene

Temp. (*t*/°C)	$^2H_0$	$^2H_1$	$^2H_2$	$^2H_3$	$^2H_4$	$^2H_5$	$^2H_6$	$^2H_7$	$^2H_8$
230	80·0	1·6	2·4	2·2	2·9	4·5	5·4	1·4	0·8
230	20·0	2·9	3·8	4·2	7·0	14·5	29·1	8·1	9·2
196	0·3	0·7	1·4	1·5	8·1	25·7	52·4	5·3	4·5

The exchange of allylic hydrogens cannot be due to an alkyl reversal mechanism, nor interconversion of alkenes and symmetrical (π) alkenyls as often postulated for exchange and isomerization of alkenes on other oxides[3a,b] and observed on ZnO by i.r. spectroscopy, with the alkenyls located at surface Zn sites.[3c] The only feasible mechanism is reversible formation of σ-bonded alkenyls and dynamic interconversion of (**1**) and (**2**) is slow, otherwise there would be concomitant double-bond shift and ready exchange of hydrogens other than vinylic and allylic. Species (**2**) are preferred on Al_2O_3[2] and thus allylic exchange may be energetically unfavourable for some compounds, due mainly to the increased bond angle required by the π systems, *e.g.*, cyclopentenyl, a restriction not present for the σ-bonded analogues.

Vinylic hydrogens are replaced by reversible formation of surface vinylic complexes, (A) or (B). Both *cis* ⇌ *trans* interconversions and double-bond shift invariably occur simultaneously on other oxides.[3] However, the two reactions clearly occur by different mechanisms on Ga_2O_3, and the distinction is due to the unusual stability of the σ-bonded alkenyls, so that even though double-bond shift in alk-1-enes is much faster than in internal olefins it is still quite slow. Since exchange of vinylic hydrogens in internal olefins occurs readily, vinyl intermediates seem responsible for *cis* ⇌ *trans* interconversions. If the double bond is weakened by $p_\pi \rightarrow p_\pi$ donor bonding to an empty p orbital of surface Ga, rotation about the double bond and thus isomerization is achieved. Also, charge donation to the surface explains the effect of electron-releasing substituents on the reactivity of vinylic hydrogens (*e.g.* the relatively inert ethylene). The bridged complex has analogues in organogallium chemistry.[4]

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